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Atomistic Predictions of Thermophysical and Mechanical Properties of HMX

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Mesomechanics models, in which the explosive grains and binder in a plastic-bonded explosive (PBX) formulation are resolved within a continuum hydrodynamic or material point method framework, are increasingly used to improve our understanding of the basic physics of PBXs subjected to various thermal or mechanical loading scenarios [1]. As the level of detail in mesomechanics models improves, there will be an ever greater demand for information about constituent properties, generally as functions of temperature, stress state, and strain rate, and frequently in regimes where direct experimental determination is extremely difficult, if not impossible [2].

Fortunately, atomistic molecular dynamics (MD) methods, judiciously applied to appropriate problems, can provide credible predictions for many of the thermophysical and mechanical properties needed to assist and/or constrain mesomechanics modelers. We have undertaken a series of classical MD and Monte Carlo simulations with the goal of providing some of the parameters needed for the successful (i.e., physically meaningful, reliable) formulation and implementation of mesomechanics models for PBXs [3-8]; the majority of the results were obtained from multinanosecond MD simulations using a flexible molecule potential-energy surface. The current emphasis is on the liquid and pure crystalline forms of HMX (β, α, and δ); relative prioritization of particular properties was based on extensive and ongoing discussions with personnel in T, X, and ESA Divisions.

Validation of the force field [5] used was achieved by comparison between measured and calculated values for:

- crystal lattice parameters (β, α, and δ);
- linear and volumetric coefficients of thermal expansion (β, α, and δ);
- heats of sublimation (β, α, and δ);
- anisotropic sound speeds for β-HMX.

Predictions were made for the following temperature dependent liquid state properties (p = 1 atm, 550 K < T < 800 K):

- thermal expansion, shear viscosity, self-diffusion [6];
- thermal conductivity [7].

Calculations of the pressure dependence of the shear viscosity

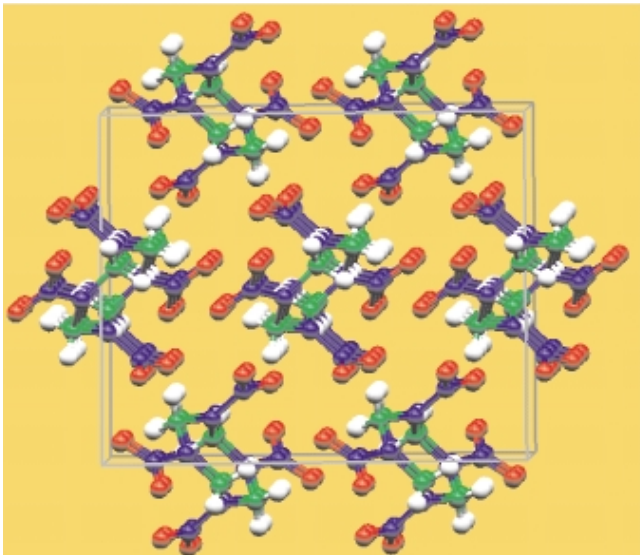

Figure: Snapshot from an isothermal-isobaric MD simulation of β-HMX.

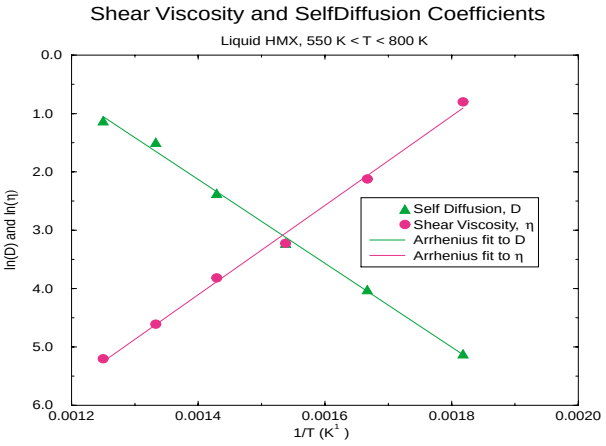

Figure: Temperature dependent shear viscosity and self-diffusion coefficients for liquid HMX.

and self-diffusion coefficients are underway for T = 800 K, p < 1.5 GPa.

Elastic limit mechanical properties that have been computed include:

- complete isothermal elastic tensors for β-, α-, and δ-HMX corresponding to room temperature and pressure, based on an analysis of the microscopic strain fluctuations obtained from isothermal-isobaric MD simulations [8];
- anisotropic sound speeds for any given direction in the crystals [5,8] (a derivative quantity calculated directly from the elastic tensor).

Knowledge of the elastic tensor allows calculation of bulk elastic properties (shear and bulk modulus) in addition to the sound speeds mentioned above; transformation between isothermal and isentropic elastic properties can be accomplished given the thermal expansion tensor. Simulations to yield the elastic tensors of β- and δ-HMX at elevated pressures and temperatures are in progress.

Careful analysis of two sets of experimental isothermal compression data for β-HMX reveals significant sensitivity of the bulk modulus to the equation of state fitting form chosen and to the domain over which the fit is performed [9]. Since neither of the experiments samples the low compressions required to determine the true zero-pressure modulus, we are performing a battery of simulations that will hopefully serve to determine which among the common fitting forms is most appropriate as well as to resolve an apparent inconsistency between the bulk modulus derived from microscopic strain fluctuations and that determined from the measured (and computed) high-pressure hydrostatic compression curve [8].

Additional simulations in progress or planned for in the near future will provide:

- specifc heat;
- Gruneisen gamma coefficient;

each as a function of pressure and temperature, and for all relevant phases.

As the level of detail in mesomechanics models improves, there will be an ever greater demand for information about constituent properties....

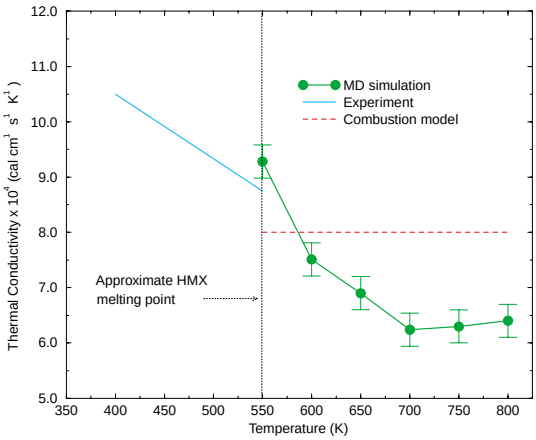

Figure: Temperature dependent thermal conductivity coefficient for liquid HMX.

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